



Removal of herbicide diuron and thermal degradation products under Catalytic Wet Air Oxidation conditions

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ARTICLE INFO

Article history:

Received 1 April 2009

Received in revised form 4 May 2009

Accepted 23 May 2009

Available online 6 June 2009

Keywords:

Waste water treatment

Diuron

Catalytic Wet Air Oxidation

Degradation products

Degradation pathways

ABSTRACT

The Catalytic Wet Air Oxidation (CWAO) of diuron (*N*-(3,4-dichlorophenyl)-*N,N*-dimethylurea), a herbicide widely used in agriculture and belonging to the phenylurea family, has been investigated in aqueous solution in the presence of a Ru/TiO₂ catalyst at 140–180 °C and 5 MPa total air pressure. Diuron and Total Organic Carbon (TOC) have been analyzed. Some reaction products were identified by LC–ES/MS, and the amount of the inorganic ions and organic products generated during the process have been measured. Thermal degradation is the main initial process yielding mainly 3,4-dichloroaniline (DCA) and dimethylamine (DMA). Further oxidations lead to ring opening and smaller organic molecules from DCA, but the DMA fragment was more difficult to eliminate. Reactions between DCA and carboxylic acids conducted to the formation of condensation products. On the other hand, dechlorination was fast and complete. The work points out that CWAO over Ru supported catalysts may not be a viable technique for degradation of diluted aqueous solutions of diuron. The mineralization is incomplete compared to other Advanced Oxidation Processes, and a possible leaching of the metal by the amines formed by thermal degradation of diuron may be critical.

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1. Introduction

With increasing use of pesticides over the last decades, there is a growing concern with the potential of contamination of surface waters and groundwater and risks to human health. Diuron [*N*-(3,4-dichlorophenyl)-*N,N*-dimethylurea] is a substituted phenylurea which is widely used in agricultural areas as a broad-spectrum herbicide for the control of a wide variety of annual and perennial broadleaf and grassy weeds [1,2]. Its mechanism of action is the inhibition of photosynthesis. It is largely used in vineyards, which constitute the major crop in some districts in France. The widespread use of diuron leads to a certain environmental impact, since diuron is dispersed in water via leaching and run-off. The environmental fate of diuron has been the subject of numerous studies [3–5]. Because of its intensive use, its low volatility and its slow biodegradation mechanism (the soil half-life is reported in the range 30–180 days), diuron and its metabolites have been frequently detected as contaminants in surface waters and groundwater [6]. Because its toxicity, diuron has now been registered in the European Union list of priority hazardous substances [7]. The diuron has been recently banned or at least strictly limited to 1.5 kg ha^{−1} in vineyards in France [8].

Therefore, to avoid the accumulation of this herbicide in the aquatic system, the development of methods for its total removal from wastewater is very important, in particular in the effluents produced in the equipments used for the treatment. After the application of diuron, the spreaders, cans, sprays and tank bottoms are usually washed and the contaminated water is dispersed on the soil. These effluents contain a higher diuron concentration than that found in natural effluents (the solubility of diuron in water is low, i.e. 42 ppm, 1.9×10^{-4} mol L^{−1} at 25 °C).

The oxidative treatment of wastewaters containing herbicides is considered as an effective method to eliminate these contaminants. Techniques designed as AOP (Advanced Oxidation Processes) characterized by “in situ” production of reactive hydroxyl radicals (*OH) under mild experimental conditions are potentially useful. In the last years, the elimination of diuron from aqueous solutions has been investigated, using photocatalysis [9–12], Fenton and photo-Fenton processes [13–17], electro-Fenton process [18,19], ozonation [20–22] ... Although the strong potential of AOP's for treating these contaminated wastewaters is widely recognized, it may be interesting to compare with other methods of degradation.

In this context, the degradation of diuron by Catalytic Wet Air Oxidation (CWAO) in the presence of a supported ruthenium catalyst is reported in this study. The published information in this research field of WAO on such a pollutant is very scarce [23]. This study has focused primarily on evaluating the degradation levels

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obtained for a saturated solution of diuron. The disappearance of the parent compound, the occurrence of intermediate products generated during treatment, the mineralization, and the release of anions and cations were measured. The degradation pathways by CWAO were determined.

The catalyst used for experiments is a Ru/TiO₂ catalyst, known from our previous studies as an active and stable catalyst in the degradation of a few model pollutants or real industrial effluents [24–30], including 2-chlorophenol and paper bleaching effluents releasing chloride ions during oxidation [25,26,29].

2. Experimental

2.1. Materials

Diuron, 3,4-dichloroaniline (DCA), dimethylamine (DMA) and *N*-(3,4-dichlorophenyl)-*N*-methylurea (DCPMU) were purchased from Aldrich–Sigma.

The support material was TiO₂ P25 (Degussa, 50 m² g^{−1}) also used for the photocatalytic study [12]. The catalyst was prepared by incipient wetness impregnation of the supports with an aqueous solution of Ru(NO)(NO₃)₃·3H₂O. The support was dried overnight in an oven at 100 °C and was impregnated with the appropriate volume of a solution containing the amount of ruthenium salt to obtain 3 wt% Ru content. The dried mixture, transferred into a tube cell, was reduced by heating up in a hydrogen flow (15 L h^{−1}) at a rate of 1 °C min^{−1} up to 300 °C, and maintaining this temperature for 2 h. After cooling under hydrogen and purging with argon, passivation of the catalyst was carried out in a flow of diluted oxygen mixture (1% O₂/N₂). The characterization of this catalyst by Transmission Electron Microscopy showed a very homogeneous distribution of the Ru particles on the support with a mean particle size of 3.3 nm [30].

2.2. Procedure

Solutions of 40 mg L^{−1} of diuron (180 μmol L^{−1}) were prepared in LC-grade water, which is close to the maximum solubility of this herbicide in water at 25 °C [6]. The initial pH was 5.9 and the Total Organic Carbon (TOC) was 19.5 ± 1 mg L^{−1}. The reaction was performed in a 300 mL batch reactor equipped with a stirrer and an electric heating jacket. The reactor was made of Hastelloy C22. The reaction temperature was maintained within ±1 °C by means of a PID controller. The operating pressure of oxidation reactor was controlled by a compressed air reservoir of 1 L. The stirring speed was set at 1000 rpm. Liquid samples of 3 mL were periodically taken by means of an internal tube connected to a valve. In the standard procedure for an oxidation experiment, the reactor was charged with 150 mL of Diuron solution (40 mg L^{−1}) and 0.2 g L^{−1} of 3% Ru/TiO₂ catalyst. The reactor content was then flushed and pressurised with argon and heated under stirring, at a rate of ca. 4 °C min^{−1}. Once the desired temperature (140 °C or 180 °C) was reached, argon was changed by air pressure to get a pressure of about 5 MPa. This point was taken as “zero time” in all experiments.

2.3. Analytical procedures

Concentrations of unreacted diuron and of its degradation products were measured by an HPLC Shimadzu LC-10 AD chromatograph equipped with a diode array detector (SPD-M10A) and a C-18 100 mm × 2 mm column (Uptisphere HDOC18) heated at 30 °C. The mobile phase was a mixture of water acidified with H₃PO₄ at pH 2.8 and methanol (50/50, v/v). The quantification was carried out at wavelength 254 nm.

The progress of mineralization of diuron was monitored by determination of Total Organic Carbon concentrations by direct

injection of the filtered samples into a Shimadzu-5050 TOC analyzer provided with a NDIR detector.

Since diuron contains two organic nitrogen and two organic chlorine atoms, formations of NH₄⁺, NO₃[−] and NO₂[−], as well as Cl[−] are expected during the reaction. The progress of DMA, inorganic anions (NO₂[−], NO₃[−], Cl[−]) and cations (NH₄⁺) formations was followed by LC-IC (Dionex) with an IonPac AS14A 250 mm × 4 mm column for anions and an IonPac CS16 250 mm × 5 mm column for cations. The eluent was 8 mmol L^{−1} of Na₂CO₃ with 1 mmol L^{−1} of NaHCO₃ for inorganic anions and acidic water with 22 mmol L^{−1} H₂SO₄ for cations, both at 1 mL min^{−1}.

Carboxylic acids were analyzed by HPLC (Prostar Varian) with a CAR-H Sarasep 300 mm × 4.6 mm column at the detection wavelength fixed at 210 nm. The eluent was acidic water (5 mmol L^{−1} H₂SO₄) at 1 mL min^{−1}.

The identification of some degradation products was performed by LC-ES/MS using a Hewlett-Packard HP 1100 system in the positive and negative ionization modes, after SPE preconcentration on prepacked cartridges (OASIS HLB).

The pH of liquid samples was measured using a pH meter (Radiometer Analytical PHM240).

The Ru concentration in the liquid phase at the end of the experiments was measured by ICP-OES (Activa, Horiba JobinYvon) to detect any leaching of the catalyst.

3. Results and discussion

3.1. Thermal degradation of diuron

The thermal instability of phenylureas has been mentioned in the literature [23,31]. Some preliminary experiments were performed to evaluate the thermal stability of diuron (180 μmol L^{−1}) at temperatures used for CWAO. The reaction mixture was analyzed at regular time of reaction by chromatography while temperature increased from room temperature to 140 °C under argon pressure at a rate of 4 °C min^{−1}. This temperature was then maintained for 2 h. After an initial small increase of diuron concentration which may be attributed to a better solubilization in the saturated solution, the concentration (180 μmol L^{−1}) decreased continuously from the temperature of ca. 140 °C until it reached less than 0.2 μmol L^{−1} after two hours. Under these experimental conditions, two main products were observed: 3,4-dichloroaniline produced by hydrolysis of diuron which was identified by HPLC and co-injection of the pure compound, and the co-product of hydrolysis dimethylamine, which was detected and analyzed by ionic chromatography. The formation of DMA occurred in parallel to the formation of DCA with similar concentrations. Both products remained relatively stable under argon at 140 °C. The *N*-demethylation product (*N*-(3,4-dichlorophenyl)-*N*-methylurea), DCPMU, often observed during AOP degradations of diuron, was only detected as traces (<0.12 μmol L^{−1}). The observations of DCA and DMA are in agreement with earlier reports that indicated a decomposition of diuron involving formation of isocyanate which subsequently hydrolyses into the amine and CO₂ [31]. A decrease of a few percent in TOC was detected after 2 h of treatment, corresponding roughly to the elimination of one molecule of CO₂ per molecule of diuron thermally decomposed. A similar degradation of diuron into DCA was described during the heating of diuron up to 180 °C in a closed vessel initially set at atmospheric pressure of air [23].

3.2. Catalytic Wet Air Oxidation of diuron at 140 °C

The Catalytic Wet Air Oxidation of an aqueous solution of diuron (180 μmol L^{−1}, 19.5 mg L^{−1} TOC) was performed at 140 °C and 5 MPa of air pressure, in the presence or absence of 25 mg 3%

Ru/TiO₂ catalyst. During the degradation of diuron, DCA and DMA were found to be the major intermediates. They resulted from the thermal decomposition of diuron. Fig. 1 shows the results for the catalyzed and uncatalyzed experiments.

Fig. 1a, giving the evolution of the concentrations of diuron and DCA as a function of time, shows that in both cases the concentration of diuron decreased from 180 $\mu\text{mol L}^{-1}$ to ca. 100 $\mu\text{mol L}^{-1}$ during the heating period, due to its thermal instability shown in the previous paragraph. After the introduction of air, disappearance of diuron was complete in less than one hour, whether a catalyst was added or not, and the pesticide was totally converted into DCA and DMA (not shown). Since this reaction is purely thermal, the degradation of diuron occurred at the same reaction rate. In the absence of the catalyst, DCA and DMA concentrations remained nearly constant with time of reaction. On the other hand, in the presence of the catalyst and air, DCA formed by thermal decomposition was oxidized, while the concentration of DMA (not shown) decreased at a much lower rate.

Fig. 1b illustrates the evolution of the experimental TOC (TOC_{exp}), in the absence or presence of the catalyst. In the uncatalyzed experiment, no appreciable decrease of the experimental TOC (TOC_{exp}) measured using the TOC analyzer was observed and the TOC_{exp} remained more or less constant at 18 mg L⁻¹. This value is consistent with a decomposition scheme of diuron to DCA, DMA and CO₂ (only one carbon is eliminated as CO₂ from the initial molecule containing nine carbons) and no further

mineralization of the degradation products in the absence of a catalyst. In the presence of the ruthenium catalyst, reduction of TOC was initially fast, which confirms the mineralization of some organics. But TOC abatement continued very slowly afterwards and its complete removal was difficult to achieve suggesting the presence of refractory products under these conditions (140 °C and 5 MPa air). TOC concentration was reduced from 19.5 mg L⁻¹ to 6.5 mg L⁻¹ after 24 h. The calculated TOC value (TOC_{cal}) was estimated from the carbon containing species (diuron, DCA, DMA, carboxylic acids...) quantified by HPLC and ionic chromatography. The difference between the two curves represents the part of unknown and/or known and non-quantified by-products during the CWAQ of diuron. More information on these by-products is available in the following paragraph.

3.2.1. Identification of the minor oxidation intermediates

HPLC analyses showed the disappearance of diuron and the formation of DCA, but the oxidation of diuron yielded also some minor degradation products from the beginning of the reaction, which in turn might disappear. They result from the oxidation of the urea group in diuron or from the oxidation of the DCA intermediate. Identification of products was made by LC–MS in the samples obtained after 1 h or 6 h of reaction, after filtration and preconcentration on a cartridge. The compounds detected are listed in Table 1.

The majority of these products was detected in positive mode ($M + 1$ and $M + 23$), while no compound was detected in negative

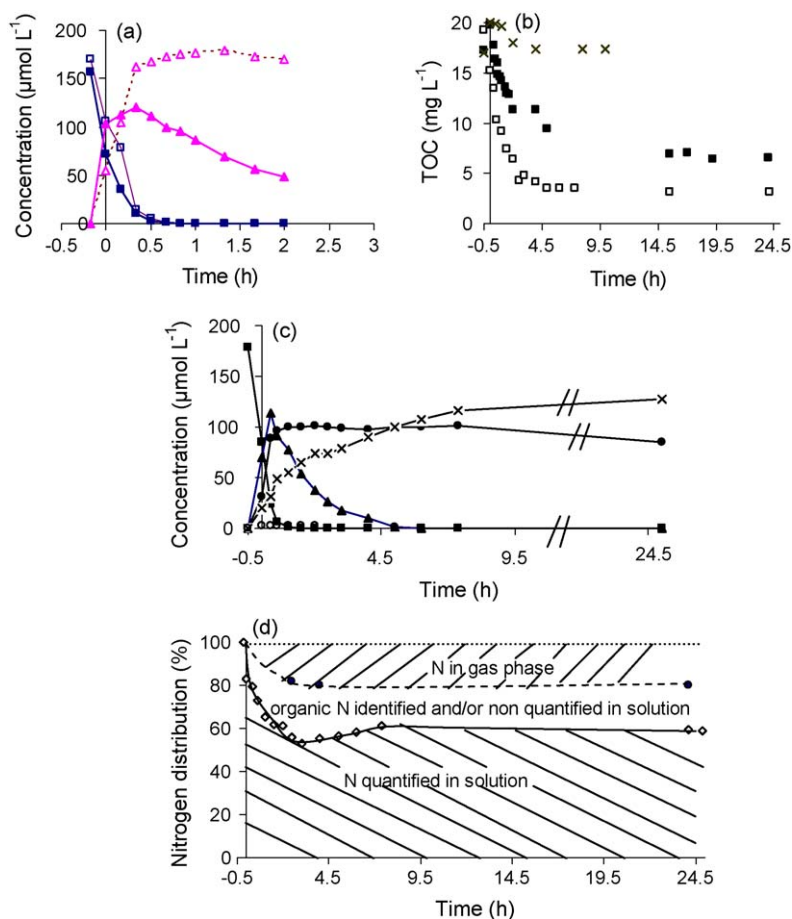
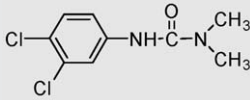
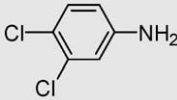
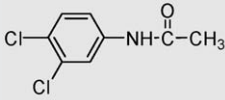
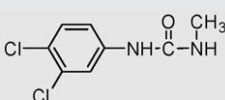


Fig. 1. Degradation treatment of diuron (150 mL, 180 $\mu\text{mol L}^{-1}$, 140 °C, 5 MPa air) in the absence of a catalyst (WAO) or in the presence of 3% Ru/TiO₂ (0.2 g L⁻¹, CWAQ). a) Concentrations of diuron (\square , \blacksquare) and DCA (\triangle , \blacktriangle) during WAO (open symbols) or CWAQ (full symbols). b) Evolutions of experimental TOC_{exp} (\times) during WAO, and of calculated TOC_{cal} (\square) and experimental TOC_{exp} (\blacksquare) during CWAQ. c) Evolutions of some N-containing organic and inorganic compounds during CWAQ: diuron (\blacksquare), DCA (\blacktriangle), DMA (\bullet), NO₃⁻ (\circ) and NH₄⁺ (\times). d) Nitrogen balance during CWAQ of diuron: nitrogen analyzed by Kjeldahl method (\bullet) and nitrogen quantified by HPLC and ionic chromatography (\diamond).

Table 1

Identification of by-products by LC–ES/MS during CWAQ of diuron at 140 °C.

ES positive $m/z = M + 1$	ES positive $m/z = M + 23$	Degradation time	Retention time (min)	Compound	MW
233/235/237	255/257/259	1 h	14.7	 diuron	232
162/164/166	–	1 h, 6 h	10.1	 DCA	161
204/206/208	–	1 h	3.0	 3,4-dichlorophenyl acetamide	203
219/221/223	–	1 h	14.0	 DCPMU	218
166/168/170	–	1 h, 6 h	4.5	?	

mode. Besides diuron, the analysis confirmed the presence of DCA ($M = 161$). The peak at $M = 218$ was assigned to 3,4-dichlorophenylmethylurea (DCPMU). This product formed from diuron by oxidation of the urea group and loss of a methyl group was also identified by comparison with an authentic sample. On the other hand, the identification of the 3,4-dichlorophenylacetamide ($M = 203$) suggests the possibility of reactions between the products formed during the reaction, such as for instance the reaction of DCA with low MW carboxylic acids, namely acetic acid in that case. The detection of this compound is in agreement with results of Oliviero et al. who studied CWAQ of aniline over a 5% Ru/CeO₂ catalyst ($T = 160$ °C, $P_{O_2} = 2$ MPa, aniline concentration = 20 mmol L⁻¹) and identified many by-products by GC–MS, including *N*-phenylacetamide [32]. Indeed, low MW carboxylic acids were detected by HPLC from the beginning of the reaction. These were oxalic acid in concentration of ca. 35 $\mu\text{mol L}^{-1}$ at total conversion of diuron, and maleic and acetic acids in much lower concentrations (0.1–0.4 $\mu\text{mol L}^{-1}$). These carboxylic acids, once formed were not further oxidized under the conditions used. Finally, the peak at retention time of 4.5 min could not be properly identified from the fragmentations. Comparisons were performed with HPLC–MS data from the photocatalysis experiments [12] or from the literature [9]. Under CWAQ conditions, no molecule corresponding to the hydroxylation of the aromatic ring or the urea moiety was observed, as often mentioned in the case of Advanced Oxidation Processes involving OH[•] radicals.

3.2.2. Fate of the heteroatoms

The diuron molecule contains two atoms of chlorine and two atoms of nitrogen. The formation of inorganic ions (NO₂⁻, NO₃⁻, NH₄⁺ and Cl⁻) was measured in the course of the reaction by ionic chromatography. The increase of the concentration of chloride ions

released was rapid at the beginning of the reaction, showing that the C–Cl bonds are easily cleaved. After 2 h and 4 h of reaction, 53% and 76% of the chlorine atoms were converted, respectively. The total amount of chloride ions produced at the end of the experiment was approximately 360 $\mu\text{mol L}^{-1}$. Taking into account the initial concentration of diuron of ca. 180 $\mu\text{mol L}^{-1}$, this means a total mineralization of the chlorine content of diuron. It is clear that chlorine is eliminated from the organic matter in the first steps of the reaction and that the residual TOC at the end of the experiment (6.5 mg L⁻¹, 67.5% mineralization) did not correspond to any chlorinated compounds.

The nitrogen mass balance of diuron degradation is more complex. Fig. 1c shows the changes in concentrations of organic compounds (diuron, DCA, and DMA) and of inorganic species (NH₄⁺, NO₂⁻ and NO₃⁻) containing nitrogen. DCPMU was only detected in traces. It is clearly shown that DCA formed by thermal decomposition was totally transformed within 6 h, whereas DMA was stable under these conditions. The main form of inorganic nitrogen in solution from DCA is NH₄⁺, whereas only traces of nitrates were detected.

The pH of the solution was found equal to 6 at the beginning of the CWAQ of diuron and decreased slowly during 5 h to reach 4. At 140 °C and after 24 h of CWAQ, the nitrogen of diuron was converted into ammonium ions (pK_a of NH₃ = 9.27) and DMA, 36 mol.% and 23 mol.% respectively. At this temperature, a weak concentration of NO₃⁻ ions was formed.

Finally, the nitrogen in solution coming from diuron, DCA, DMA, DCPMU, NH₄⁺ and NO₃⁻ was calculated and compared to the experimental measure by the Kjeldahl method of nitrogen in solution of some samples. This latter method analyses the total amount of organic nitrogen and ammonium ions in solution. So, the difference between NH₄⁺ quantified by ionic chromatography and Kjeldahl nitrogen leads to a measure of nitrogen-containing

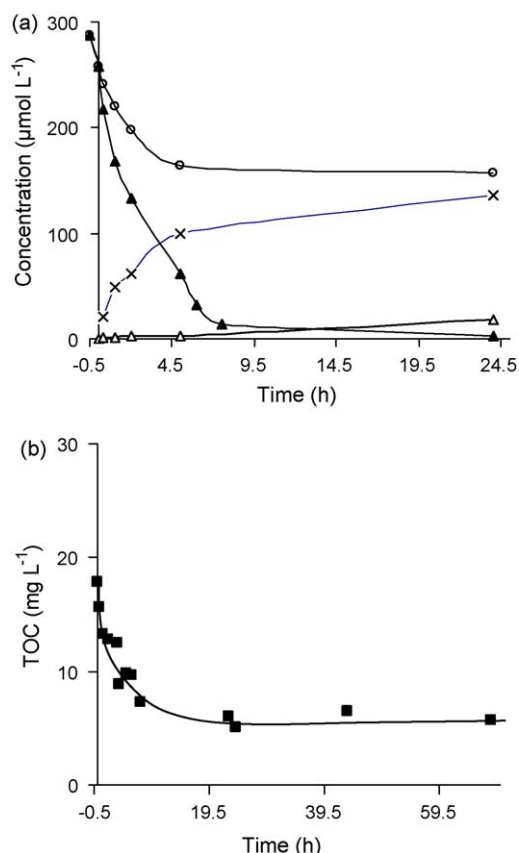


Fig. 2. CWAO of DCA ($290 \mu\text{mol L}^{-1}$, 140°C , 5 MPa air, 0.2 g L^{-1} of 3% Ru/TiO₂). a) Evolutions of DCA (\blacktriangle), NH_4^+ (\times), NO_3^- (\triangle) and nitrogen balance (\circ) as a function of time; b) TOC abatement as a function of time.

compounds present in solution which could not be quantified by chromatography. Also, the difference between the initial nitrogen content (ca. $360 \mu\text{mol L}^{-1}$) and the Kjeldahl value may be a rough measure of nitrogen evolved in the gas phase. Fig. 1d shows the nitrogen distribution as a function of time. The balance of nitrogen indicates 60% of organic and inorganic nitrogen identified by HPLC and ionic chromatography. Further experimental measure as the Kjeldahl method shows that the only part of the non-analyzed nitrogen is in the liquid phase after 24 h. 80% of nitrogen are in the liquid phase and 20% of initial nitrogen content may have been converted into N_2 in gas phase. N_2 formation seems probable, since different authors have explained the incomplete conversion of nitrogen-containing compounds by the formation of N_2 during CWAO [33–36]. It is not excluded that some of the nitrogen-containing organics are adsorbed on the catalyst [32].

3.2.3. CWAO of DCA at 140°C

3,4-Dichloroaniline DCA is one of the main intermediate compounds when diuron is thermally treated by CWAO. Tests of toxicity on *vibrio fischeri* bacteria and on protozoaires have shown a higher toxicity for DCA than for diuron [4,37]. It is then important to better understand the conditions and ways of degradation of this metabolite. CWAO experiments were carried out using aqueous solutions containing $290 \mu\text{mol L}^{-1}$ of DCA ($\text{TOC} = 21 \text{ mg L}^{-1}$). Fig. 2 shows the degradation (Fig. 2a) and mineralization (Fig. 2b) of DCA as a function of time. During the heating period under the inert atmosphere, the DCA concentration decreased slightly. After the introduction of oxidant atmosphere (5 MPa of air), DCA was successfully eliminated from the reaction medium within 8 h of treatment. The carbon content was essentially mineralized to CO_2 during this period, as shown by the large decrease in TOC measured

from 21 mg L^{-1} to 6 mg L^{-1} . Then, the TOC conversion remained stable at 74% over a 60 h period. This lack of TOC conversion was attributed to the formation of refractory compounds that we tried to identify.

Different carboxylic acids were identified during the CWAO degradation of DCA, among these compounds oxalic and maleic acids were quantified with a maximum concentration of 16 and $3 \mu\text{mol L}^{-1}$, respectively. As in the case of diuron treatment, the concentration of oxalic acid was higher ($16 \mu\text{mol L}^{-1}$) than the concentration of maleic acid ($3 \mu\text{mol L}^{-1}$). Only traces of acetic acid were detected after 1 h of degradation. In our conditions (140°C , 50 bar), these carboxylic acids were not degraded in presence of the 3% Ru/TiO₂ catalyst. Studies concerning the wet air oxidation of aromatic compounds (aniline, substituted phenols...) reported the formation of different carboxylic acids (acetic, maleic, formic...) in agreement with our results [36,38–40]. Higher temperatures are required for the elimination of maleic acid, which may explain the resistance of this acid [41]. But the presence of oxalic acid was not mentioned. The degradation of oxalic acid at $235 \mu\text{mol L}^{-1}$ was carried out in the same conditions and its rapid disappearance was observed within 90 min. The identification of oxalic acid during diuron and DCA degradations would be due to competitive adsorption on the catalyst surface, or to a higher rate of formation than the rate of mineralization.

The residual TOC at the end of the experiment (Fig. 2b) cannot be explained by the acids alone. Other refractory products were detected by HPLC and LC–MS analyses allowed to the identification of some of them. In some cases, the MS data were compared to those obtained previously. The detection and identification of the oxidation products from DCA after 6 h of reaction are described in Table 2. These products were detected both in negative and positive modes.

Some of these compounds were already detected during the degradation of diuron (e.g. 3,4-dichlorophenylacetamide), but the presence of both 3,4-dichlorophenol and 3,4-dichloroformamide was revealed. As previously observed during the degradation of diuron, condensation compounds with molecular weights in the range $291\text{--}322 \text{ g mol}^{-1}$ were also detected. The formation of these different intermediate compounds will be shortly commented.

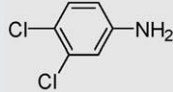
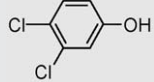
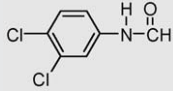
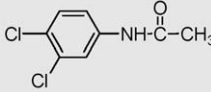
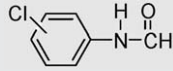
3,4-Dichlorophenol is formed by oxidative removal of the amino group followed by hydroxylation. This finding is in line with different studies on WAO of aniline [32,42]. Studies dealing with the degradation of phenylureas by Advanced Oxidation Processes also detected phenolic compounds due to the hydroxyl radicals attacks [9,43–46]. This phenolic compound will then undergo ring cleavage.

The intermediates with retention times 14.8 and 15.9 min have been identified by LC–MS as 3,4-dichlorophenylacetamide and 3,4-dichlorophenylformamide, respectively. During the degradation of diuron, only the former was detected, probably because of higher concentrations of 3,4-DCA used in these experiments. These intermediates are formed by reaction of DCA with two by-products, namely acetic acid and oxalic acid. After one hour, the pH of the reaction medium is about 6. Considering the pK_a s (aniline 2.85, acetic acid 4.76, oxalic acid 1.25 and 4.27) the reaction which may occur is a reaction of the carboxylates onto the molecular form of DCA, as shown in Fig. 3. Similarly, Oliviero et al., observed the formations of phenyl formamide and phenylacetamide during the CWAO of aniline, using a Ru/CeO₂ catalyst [32].

The detection of masses 154/156 in negative mode by LC–MS identifies phenylamide monochlorinated in position 3 or 4 (3 or 4-chlorophenylamide), but this kind of analysis does not allow the determination of the chlorine position on the aromatic ring (Table 1). Nevertheless, the loss of a chlorine atom without substitution on the ring suggests a thermal degradation of the C–Cl link and not a hydroxyl radical attack.

Table 2

Identification of by-products by LC-ES/MS after 6 h of CWAQ of DCA.

ES positive $m/z = M + 1$	ES positive $m/z = M + 23$	ES negative $m/z = M - 1$	Number isomers	Retention time (min)	Compound	MW
162/164/166			1	10.1		161
		161/163/165	1	>20		162
190/192/194		188/190/192	2	14.8		189
				6.7		
204/206/208		202/204/206	2	15.9		203
				3.0		
		154/156	1	4.1		155
		204/206	1	16.1	?	205
166/168/170		–	1	4.5	?	
		290/292/294/296	1	5.4	?	291
		256/258/260	1	9.5	?	257
		321/323/325/327	1	8	?	322

Three intermediates corresponding to the following molar mass 291, 257 and 322 g mol^{−1} were only detected in negative mode. These masses suggest the possible presence of condensation products, as already observed during degradation of diuron, but their structure was not identified. The study of aniline by Oliviero et al. showed the presence of numerous condensed oligomers like azobenzene, azoxybenzene, hydrazobenzene, oxalinide, phenazine, acridinamine, and formamido-acridine (Scheme 1) [32]. None of the high molecular weight compounds detected in our case corresponded to these condensed oligomers containing 1–4 chlorine atoms or not, hydroxylated or not.

The few products identified are not commercial, so we could not quantify their concentration. Nevertheless, the amount of non-quantified known and/or unknown products reached 6 mg L^{−1} of TOC after 24 h, i.e. 28% of the initial TOC.

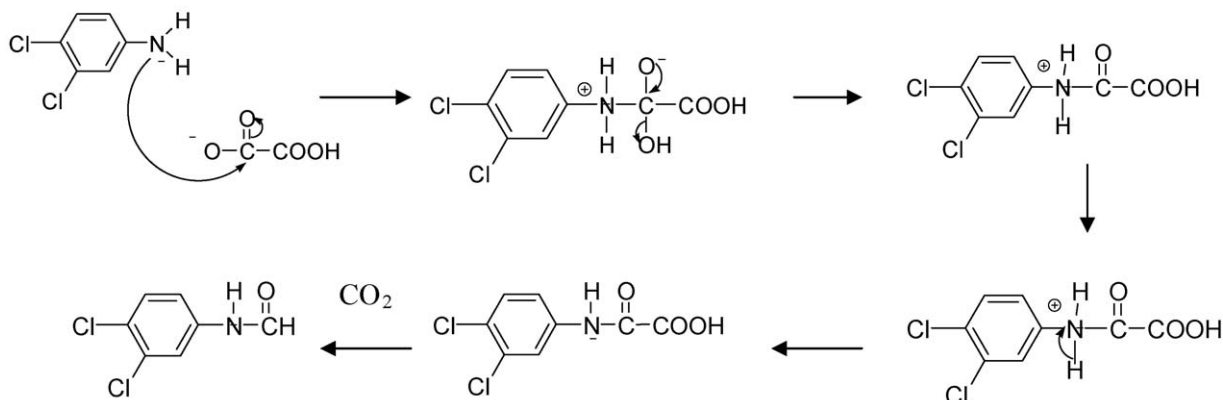
The degradations of nitrogen and chlorine heteroatoms were analyzed during the CWAQ of DCA. The concentration of chloride ions quickly increased with reaction time and the totality of chlorine atoms in DCA was released as chloride. Regarding nitrogen, DCA was completely eliminated after 24 h of reaction yielding 47% ammonium ions and 11% nitrates. The balance to 100% is attributed to the presence of unknown organic products in the reaction medium, to nitrogen adsorbed on the catalyst, and to the formation of molecular nitrogen. NH₄⁺ was the main form of inorganic N in solution, which highlights the high selectivity of transformation of DCA nitrogen into NH₄⁺. Once formed, ammonium ions are not converted under the reaction conditions used (140 °C, Ru/TiO₂ catalyst) in accordance with published studies

[35,38,47,48]. Indeed, Reddy et al. showed that the selectivity of CWAQ of aniline over a Ru/SiO₂ catalyst under 3.5 MPa of air was dependent on temperature [38]. Below 200 °C ammonium ions were mainly formed, while higher temperature above 210 °C yielded more nitrates. The late presence of nitrates would be due to the oxidation of NH₄⁺ into NO₃[−]. The pH initially of 6 decreased rapidly to pH ca. 4 with the conversion of DCA. No ruthenium leached from the catalyst was detected at the detection limit of 0.1 mg L^{−1}.

3.2.4. CWAQ of DMA at 140 °C

DMA is the other main intermediate formed by thermal degradation of diuron. The CWAQ of DMA was studied at 140 °C and 5 MPa, using a concentration of 300 μmol L^{−1} (7.2 mg L^{−1} TOC) in the presence of 0.2 g L^{−1} of the ruthenium catalyst. At 140 °C, the degradation of DMA was not complete after 24 h of CWAQ, 20.4% of initial concentration were still present in the solution. This observation agrees with results previously reported for diuron treatment. During the CWAQ experiment of diuron at 140 °C, DMA was degraded at a much lower rate than DCA. After 24 h of oxidative treatment, the degradation of DMA yielded methylamine (MA), ammonium ions, nitrite and nitrate ions in different proportions, 14.2%, 22.8%, 16% and 26.6%, respectively. This amounted to 1.6 mg L^{−1} of TOC in the final solution. The nitrogen balance was nearly complete, which means that the degradation of DMA did not yield molecular nitrogen at 140 °C. So, nitrogen in the gas phase produced during diuron oxidation originates only from the degradation of DCA amine function. The

Formation of 3,4-dichlorophenylamide



Formation of 3,4-dichlorophenylacetamide

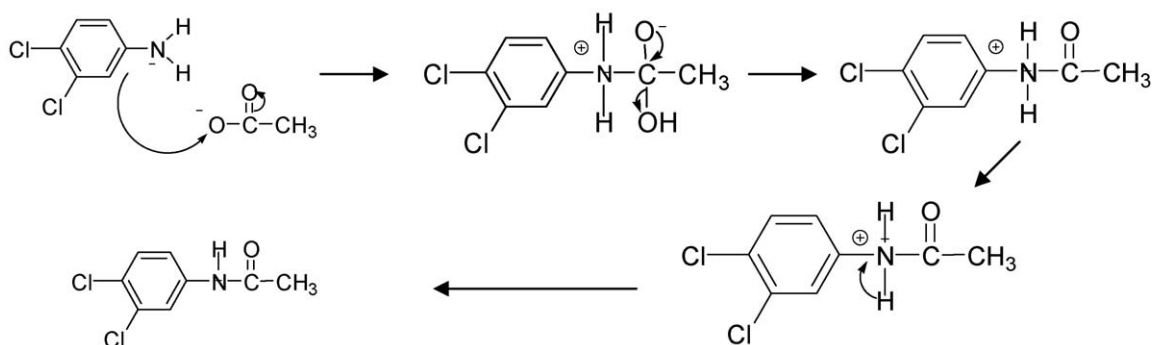
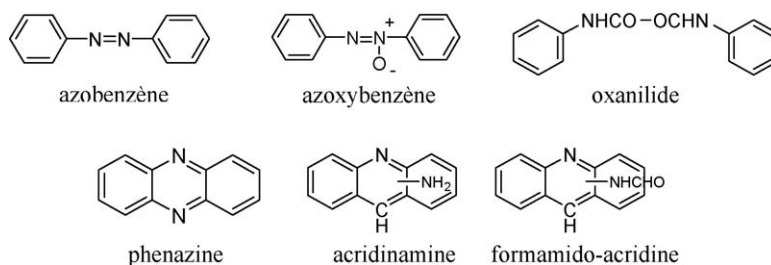


Fig. 3. Mechanisms proposed for the formations of 3,4-dichlorophenylamide and 3,4-dichlorophenylacetamide.



Scheme 1.

final solution was analyzed by ICP-AES. A concentration of 0.18 mg L^{-1} of Ru was revealed indicating that 3% of initial ruthenium has been leached from the catalyst. Further studies with higher concentrations would be necessary to determine the responsible for this leaching.

3.3. CWAOs of DMA and diuron at 180°C

Finally, CWAO of DMA ($300 \mu\text{mol L}^{-1}$) was carried out at 180°C in order to improve mineralization. During heating up to 180°C , 63% of DMA were thermally degraded to give methylamine essentially. Then with introduction of air, the complete DMA destruction was observed within 5 h at 180°C compared to 20.4% after 24 h at 140°C . Methylamine, ammonium ions and nitrates were analyzed. Compared to 140°C , the use of a higher temperature greatly increased the formation of nitrates from MA and NH_4^+ , which represented 87% of initial nitrogen at the end of the experiment.

In view of the results on DMA oxidation, experiments were carried out at 180°C in order to improve diuron mineralization.

The results are shown Fig. 4. Consistent with the results observed previously, during the heating period, diuron was completely converted into DCA, DMA and MA. After introduction of air, DCA was totally degraded after 2 h at 180°C , whereas the degradation of DMA was incomplete and slower. After 19 h of reaction, TOC

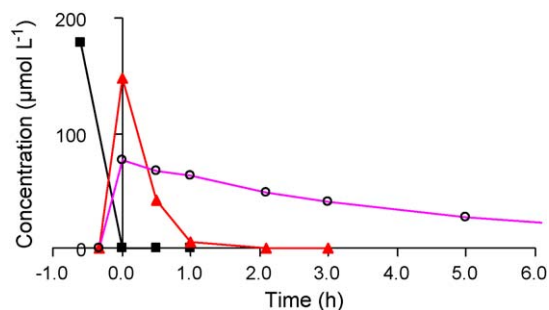


Fig. 4. CWAO of diuron at 180°C and 5 MPa air in the presence of 0.2 g L^{-1} of 3% Ru/TiO₂ catalyst: (■) diuron, (▲) DCA and (○) DMA.

- [4] C. Maluech-Brugere, G. Grizard, P. Boule, D. Boucher, *Andrologie* 11 (2001) 69–75.
- [5] D.C. Gooddy, P.J. Chilton, I. Harrison, *Sci. Total Environ.* 297 (2002) 67–83.
- [6] H. Kidd, D.R. James (Eds.), *The Agrochemical Handbook*, 3rd ed., Royal Society of Chemistry Information Series, Cambridge, UK, 1991.
- [7] European Commission, Decision No. 2455/2001/EC, of the European parliament and of the Council of 20 November 2001, establishing the list of priority substances in the field of water policy and amending, Directive 2000/60/EC, Off. J. Eur. Commun. (December 15, 2001) 331/1.
- [8] Journal Officiel No. 116–19/05/02. Official Journal of the French Republic, no. 116 du 19 mai 2002. Avis aux détenteurs d'autorisations de mise sur le marché, aux distributeurs et aux utilisateurs de produits phytopharmaceutiques contenant du diuron, p. 9362.
- [9] S. Malato, J. Caceres, A.R. Fernandez-Alba, L. Piedra, M.D. Hernando, A. Agüera, J. Vial, *Environ. Sci. Technol.* 37 (2003) 2516–2524.
- [10] M. El Madani, C. Guillard, N. Perol, J.M. Chovelon, M. El Azzouzi, A. Zrineh, J.M. Herrmann, *Appl. Catal. B* 65 (2006) 70–76.
- [11] D. Bamba, P. Atheba, D. Robert, A. Trokourey, B. Dongui, *Environ. Chem. Lett.* 6 (2008) 163–167.
- [12] M. Carrier, C. Guillard, M. Besson, C. Bordes, H. Chermette, *J. Phys. Chem. A* 113 (2009) 6365–6374.
- [13] P. Mazellier, M. Bolte, *Int. J. Environ. Anal. Chem.* 70 (1998) 163–176.
- [14] H. Gallard, J. De Laat, *Chemosphere* 4 (2001) 405–413.
- [15] P. Mazellier, B. Sulzberger, *Environ. Sci. Technol.* 35 (2001) 3314–3320.
- [16] F.J. Benitez, F.J. Real, J.L. Acero, C. Garcia, E.M. Llanos, *J. Chem. Technol. Biotechnol.* 82 (2007) 65–73.
- [17] M. Lapertot, S. Ebrahimi, S. Dazio, A. Rubinelli, C. Pulgarin, *J. Photochem. Photobiol., A* 186 (2007) 34–40.
- [18] M.C. Edelahe, N. Oturan, M.A. Oturan, Y. Padellec, A. Bermond, K. El Kacemi, *Environ. Chem. Lett.* 1 (2004) 233–236.
- [19] N. Oturan, S. Trajkovska, M.A. Oturan, M. Couderchet, J.J. Aaron, *Chemosphere* 73 (2008) 1550–1556.
- [20] M.I. Maldonado, S. Malato, L.A. Perez-Estrada, W. Gernjak, I. Oller, X. Domenech, J. Peral, *J. Hazard. Mater.* 138 (2006) 363–369.
- [21] M.J. Farre, M.I. Franch, J.A. Ayllon, J. Peral, X. Domenech, *Desalination* 211 (2007) 22–33.
- [22] J. Feng, Z. Zheng, J. Luan, J. Zhang, L. Wang, *Sci. Health, Part B: Pestic. Food Contam. Agric. Wastes* 43 (2008) 576–587.
- [23] F. Lala, C. Joannis-Cassan, A. Isambert, G. Durand, *Récents Progrès en Génie des Procédés* 90 (2003) 549–556.
- [24] J.C. Béziat, M. Besson, P. Gallezot, S. Durecu, *J. Catal.* 182 (1999) 129.
- [25] A. Pintar, M. Besson, P. Gallezot, *Appl. Catal. B* 30 (2001) 123–139.
- [26] A. Pintar, M. Besson, P. Gallezot, *Appl. Catal. B* 31 (2001) 275–290.
- [27] M. Besson, P. Gallezot, *Top. Catal.* 33 (2005) 101–108.
- [28] D. Pham Minh, P. Gallezot, S. Azabou, S. Sayadi, M. Besson, *Appl. Catal. B* 84 (2008) 749–757.
- [29] N. Li, C. Descorme, M. Besson, *Appl. Catal. B* 71 (2007) 262–270.
- [30] D. Pham Minh, G. Aubert, P. Gallezot, M. Besson, *Appl. Catal. B* 73 (2007) 236.
- [31] S. Salvestrini, P. Di Cerbo, S. Capasso, *Chemosphere* 48 (2002) 69–73.
- [32] L. Oliviero, H. Wahyu, J. Barbier, D. Duprez, J.W. Ponton, I.S. Metcalfe, D. Mantzavinos, *TranslChem* 81 (Part A) (2003) 384–392.
- [33] O.J. Hao, K.K. Phull, *Environ. Sci. Technol.* 27 (1993) 1650–1658.
- [34] C. Deiber, J.N. Foussard, H. Debellefontaine, *Environ. Pollut.* 96 (1997) 311–319.
- [35] L. Oliviero, J. Barbier, D. Duprez, *Appl. Catal. B* 40 (2003) 163–184.
- [36] J. Barbier Jr., L. Oliviero, B. Renard, D. Duprez, *Top. Catal.* 33 (2005) 77–86.
- [37] C. Tixier, M. Sancelme, F. Bonnemoy, A. Cuet, H. Veschambre, *Environ. Toxicol. Chem.* 20 (2001) 1381–1389.
- [38] G.R. Reddy, V.V. Mahajani, *Ind. Eng. Chem. Res.* 44 (2005) 7320–7328.
- [39] Y. Kojima, T. Fukuta, T. Yamada, M.S. Onyango, E.C. Bernardo, H. Matsuda, K. Yagishita, *Water Res.* 39 (2005) 29–36.
- [40] S.G. Pouloupoulos, C.A. Korologos, A. Boulamant, C.J. Philippopoulos, *Water Res.* 41 (2007) 1263–1268.
- [41] A. Pintar, G. Bercic, M. Besson, P. Gallezot, *Appl. Catal. B* 47 (2004) 143–152.
- [42] H.T. Gomes, B.F. Machado, A. Ribeiro, I. Moreira, M. Rosario, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, J. Hazard. Mater. 159 (2008) 420–426.
- [43] E. Pramauro, M. Vincenti, V. Augugliaro, L. Palmisano, *Environ. Sci. Technol.* 27 (1993) 1790–1795.
- [44] A. Amine-Khodj, A. Boulkamh, P. Boule, *Photochem. Photobiol. Sci.* 3 (2004) 145–156.
- [45] M. Canle López, M.I. Fernández, S. Rodríguez, J.A. Santaballa, S. Steenken, E. Vulliet, *ChemPhysChem* 6 (2005) 2064–2074.
- [46] K. Macounova, H. Krysova, J. Ludvik, J. Jirkovsky, *J. Photochem. Photobiol., A* 156 (2003) 273–282.
- [47] D.K. Lee, J.S. Cho, W.L. Yoon, *Chemosphere* 61 (2005) 573–578.
- [48] T.L. Gunale, V.V. Mahajani, *J. Chem. Technol. Biotechnol.* 83 (2008) 1154–1162.